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(54) Title: METHOD OF INCREASING THE SPF RATING AND COMPOUNDS SUITABLE FOR INCREASING THE SPF RATING OF FIBRE OR FABRIC (57) Abstract A method of increasing the SPF rating of a fibre or fabric, comprising the steps of providing a UVR absorber, applying the UVR absorber to a fabric having a density of less than 200 grams per square metre, whereby the UVR absorber is attached to the fibre and an application of less than 3 % UVR absorber on weight of fibre produces an SPF rating of greater than 20 for the UVR absorber and fabric combination.		

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Method of Increasing the SPF Rating and Compounds
Suitable for Increasing the SPF Rating of Fibre or Fabric
Technical Field

The present invention relates to a method of
5 increasing the sun protection factor (SPF) rating and
compounds suitable for increasing the SPF rating of fibre
or fabric.

Background of the Invention

Last year over 1,000 Australians died of skin cancer
10 while two thirds of the Australian population will
develop some form of skin cancer at some stage in their
lives. This year it is anticipated that 150,000
Australians will go to their doctors for the examination
and treatment of some form of sun induced skin cancer.

15 It is interesting to note that, in spite of public
education campaigns and the widespread use of "Sun-Block"
creams, skin cancer rates have not changed in recent
years.

Even though there has been various sun protection
20 aids in the market for many years, the present inventors
have found that most consumers do not fully understand
what an SPF rating means.

A typical fair skinned person, on a summers day in
Australia, at noon (1:00pm Eastern Summer Time), would
25 "burn" in approximately 15 minutes (ie 0.25 hours). If
this person applied "sun block" cream (or textile) of SPF
4 (if available), then this person would burn in 4 times
15 minutes, viz 1 hour. It is important to note,
however, that this person would have received the same
30 total UVR dose either way.

A common way of avoiding sunburn when performing
activities in a sunny environment is to apply a sunburn
cream to skin. The problem with such a solution however
is that most sunburn creams only provide UVR protection
35 up to an SPF rating of 15+ and therefore prolonged
exposure to the sun can still cause damage to a persons
skin despite the use of a sunburn cream.

In addition, avoiding exposure of skin to the sun by

wearing clothing, for example a T-shirt, does not necessarily provide adequate UVR protection for the wearer, when the wearer is exposed to the sun for prolonged periods. This problem is compounded by the
5 fact that in hot climates it is desirable to have light weight clothing, which typically has a low SPF rating.

For example, for materials having a density of less than 200 grams per square metre, nylon has an SPF rating of between 10 and 15, polyester has an SPF rating of
10 between 13 and 17, wool has an SPF rating of 10-20 and cotton has an SPF rating of between 5 and 15. It follows therefore that a person wearing a shirt made of light weight fabric such as cotton or wool, if exposed to the sun for prolonged periods can still be subjected to
15 significant doses of UVR radiation. Thus, over an extended period of time, a person working in the sun and wearing a cotton T-shirt can still be exposed to a significant cumulative dose of UVR radiation.

Essentially, the SPF protection of a fabric depends on
20 the "Cover Factor" of the fabric. The Cover Factor may be defined as the percentage of the fabric surface that is covered by the yarns of the fabric. If one assumes that the yarns employed to weave or knit the fabric are completely opaque to UVR radiation (which is not the case
25 in reality) then the fabric SPF would be simply related to Cover Factor by the following formula:

$$\text{Fabric SPF} = \frac{100}{100 - \text{Cover Factor}}$$

Disclosure of the Invention

30 In one aspect, the present invention provides a method of increasing the SPF rating of a fibre or fabric, comprising the steps of providing a UVR absorber, applying the UVR absorber to a fabric having a density of less than 200 grams per square metre, whereby the UVR
35 absorber is attached to the fibre and an application of less than 3% UVR absorber on weight of fibre produces an SPF rating of greater than 20 for the UVR absorber and fabric combination.

In one embodiment, the present invention provides a method of increasing the SPF rating of a fibre or fabric, comprising the steps of providing a UVR absorber, applying the UVR absorber to a fabric having a density of
5 less than 200 grams per square metre, whereby the UVR absorber is attached to the fibre and an application of less than 2% UVR absorber on weight of fibre produces an SPF rating of greater than 20 for the UVR absorber and fabric combination.

10 Preferably the UVR absorber enters the fibre and fixes itself to the fibre.

It is preferred that the combination of fabric and UVR absorber is water-fast so that washing of the fabric after its SPF rating has been increased by the addition
15 of the UVR absorber, does not cause any significant drop in the SPF rating of the fibre.

Preferably the UVR absorber comprises a substituted benzotriazole.

The fibre may be wool, nylon, polyester, cotton or
20 any other synthetic fibre or composite thereof.

It is preferred that when the fibre is nylon the UVR absorber is Fadex F (registered trade name of Sandoz).

It is preferred that when the fibre is polyester, the UVR absorber is Fadex F (registered trade name of
25 Sandoz).

Preferably the SPF rating is increased by greater than 30 for non-composite fabrics and by greater than 9 for composite fabrics.

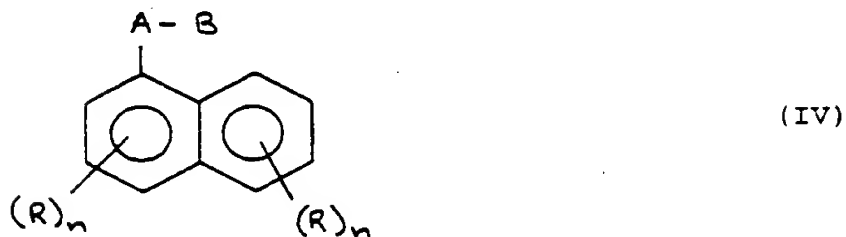
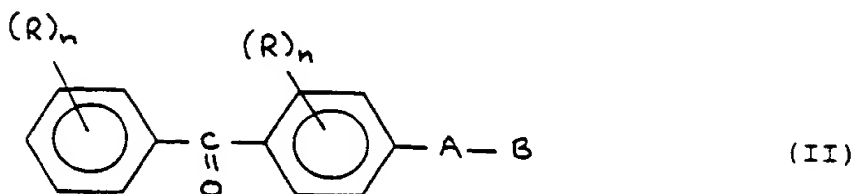
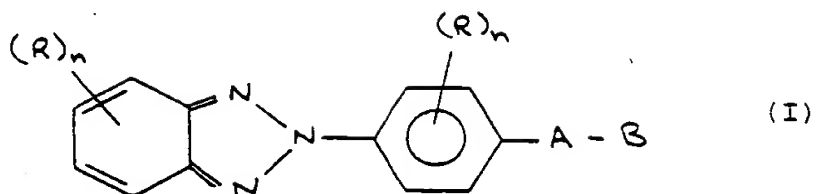
It is preferred that when the fibre is wool the UVR
30 absorber is CIBAFast W (registered trade name of CIBA-GEIGY).

It is preferred that when the fibre is a secondary cellulose acetate or triacetate, the UVR absorber is Fadex F (registered trade name of Sandoz).

35 In a second aspect, the present invention provides a method of increasing the SPF rating of cellulosic or protein fibre or fabric, comprising applying to cellulosic or protein fibre or fabric one or more

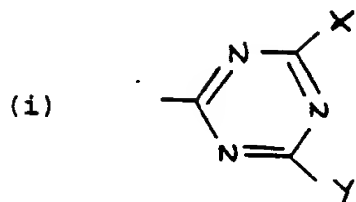
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compounds of formula (I)-(IV):



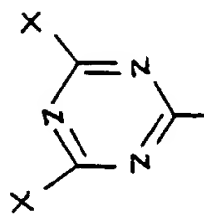
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wherein A is -NH- or -SO₂- and when A is -NH-, B is selected from a compound of formula (i) - (vii) as follows:

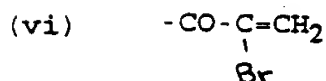
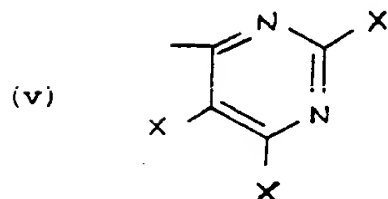
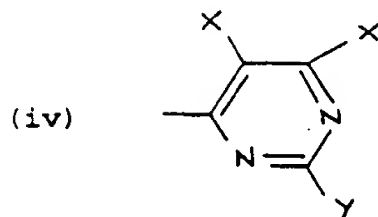
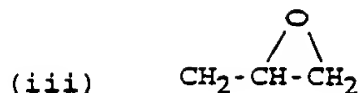


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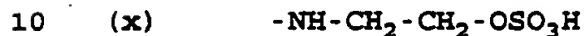
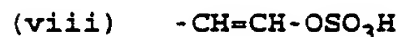
(ii)



SUBSTITUTE SHEET



and where A is -SO2-, B is selected from a compound of formulae (viii) - (x) as follows:



wherein R is independently selected from -OH, -NH2, -SO3^-, M^+, -SO3H, alkyl, alkoxy, alkanoyl, alkylcarboxylate, -S- alkyl, -CF3, -N-di-alkyl;

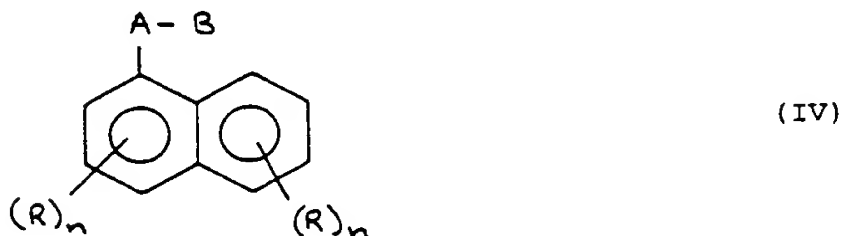
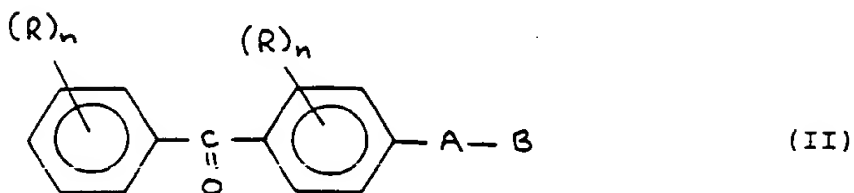
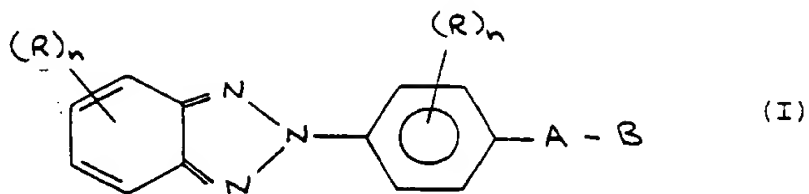
$n = 0, 1, 2, 3$ or 4

15 M^+ = cation

X = H, or Cl, F, Br and is independently selected

Y = X or R.

In a third aspect, the present invention provides a compound of formula (I), (II), (III) or (IV)



wherein A, B, R and n are as defined above;

but excluding the compound of formula (III) where A is -NH-, B is a compound of formula (ii);

10 X is Cl, n is 2 and one R is in the 3-position of the phenyl ring and is -CH₃ and the other R is in the 4-position and is -SO₃⁻ Na⁺.

In a fourth aspect, the present invention provides a process of preparing a compound of formula (I)-(IV) which
15 comprises:

- 1) for preparing compounds of formula (I)-(IV) where A is -NH- and B is a compound of formula (i), (ii), (iii), (iv) or (v):

reacting the appropriate amine of formula (I), (II), (III) or (IV) with a chloro derivative of a compound of formula (i), (ii), (iii), (iv) or (v);

- 5 2) for preparing compounds of formula (I)-(IV) wherein A is -NH- and B is a compound of formula (vi) or (vii):

10 (i) reacting the appropriate amine of formula (I), (II), (III) or (IV) with -CH₂BrCHBrCOCl to provide the dibromopropionyl derivative;

15 (ii) debromination with potassium hydroxide or the like to provide the bromoacrylamido derivative of formula (vi); and

 (iii) further debromination with potassium hydroxide or the like to provide the acrylamido derivative of formula (vii);

- 20 3) for preparing compounds of formula (I)-(IV) where A is -SO₂- and B is a compound of formula (viii) or (ix):

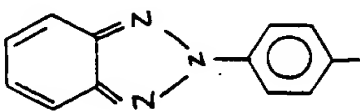
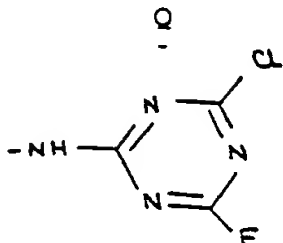
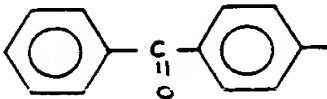
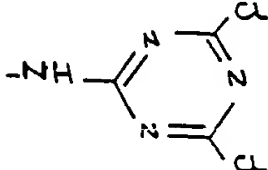
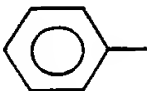
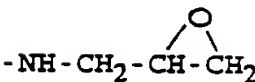
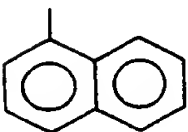
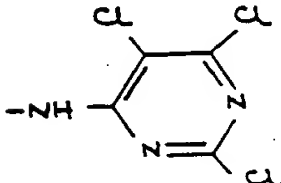
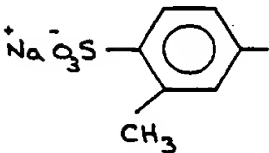
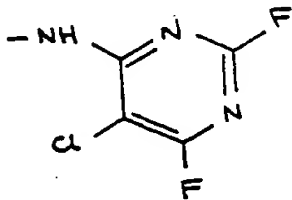
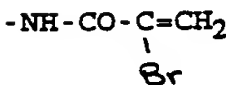
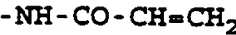

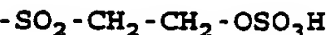
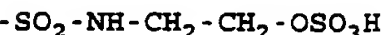
25 (i) esterification of the appropriate β-hydroxyethyl sulphone derivatives of the compounds of formulae (I) to (IV) with sulphuric acid or the like to provide compounds of formula (I) to (IV) where B is a compound of formula (viii) and;

 (ii) dehydration in the presence of a base to form the vinyl compound of formula (ix);

- 30 4) for preparing compounds of formula (I)-(IV) where A is -SO₂- and B is a compound of formula (x):

35 esterification of the appropriate β-hydroxyethyl aminosulphone derivative of the compounds of formulae (I)-(IV) with sulphuric acid or the like (as in 3(i) above) to provide compounds of formula (I)-(IV) where B is a compound of formula (x).

Preferred compounds of formula (I)-(IV), designated as P-Q for convenience is a combination of P with any Q as follows:

- | | P | | Q |
|-------|---|-----|---|
| 1. |  | 1. |  |
| 2. |  | 2. |  |
| 3. |  | 3. |  |
| 10 4. |  | 4. |  |
| 5. |  | 5. |  |
| | | 6. |  |
| | | 7. |  |
| | | 8. |  |
| | | 9. |  |
| | | 10. |  |

The starting materials for the above processes 1 to 4 are known compounds and are readily available. Given the compounds to be reacted, the skilled addressee would be able to readily determine the reaction conditions.

5 Compounds of formulae (I)-(IV) are useful as UVR absorber compounds and can be applied to fabrics of any weight. Typically, they are suitable for application to light weight summer fabrics and to heavier fabric up to and including industrial weight fabrics.

10 In a fifth aspect, the present invention provides a method of increasing the SPF rating of cellulosic or protein fibre or fabric, comprising the steps of applying a compound of formula (I)-(IV) to cellulosic or protein fibres or fabric having a density of less than 200g/m^2
15 whereby an application of less than 3% of a compound of formula (I)-(IV) on weight of fibre or fabric produces an SPF rating of greater than 20.

 In another embodiment, the present invention provides a method of increasing the SPF rating of
20 cellulosic or protein fibre or fabric, comprising the steps of applying a compound of formula (I)-(IV) to cellulosic or protein fibres or fabric having a density of less than 200g/m^2 whereby an application of less than 2% of a compound of formula (I)-(IV) on weight of fibre
25 or fabric produces an SPF rating of greater than 20.

 Cellulosic fibres may be any fibres of plant origin such as cotton, viscose, flax, linen, rayon or the like or composites thereof. Also, composites can be with polyester, polyamides, polyacrylonitriles or the like.

30 Protein fibres may be any fibres of animal origin such as wool, mohair, silk, cashmere, angora or the like or composites thereof. Also, composites can be with polyester, polyamide or the like.

 It is preferred that when the fibre is protein, a
35 compound of formula (I)-(IV) where B is (ii), (iv), (v), (vi), (vii), (viii) or (ix) is applied.

 It is preferred that when the fibre is cellulosic, a compound of formula (I)-(IV) where B is (i), (ii), (iii)

or (iv) is applied.

Preferably, the cellulosic fibre is cotton and the protein fibre is wool.

Typically, a 2% on weight of fibre application of compound of formula (III) will increase the SPF rating of a 120g/m² 100% cotton fabric from 15+ to 30+.

Typically, a compound of formula (I)-(IV) enters the fibre and fixes itself to the fibre with the reactive group B of compounds of formula (I)-(IV) reacting with the fibre.

Typically, for composite fabrics, sequential application of UVR absorber relevant for each component of the composite increases the SPF rating of the composite fabric by greater than 30.

For example, for cotton/polyester fabric, sequential application of UVR absorber for cotton followed by the application of UVR absorber for polyester or vice versa, increases the SPF rating of the fabric by greater than 30.

In a sixth aspect, the present invention provides an article of clothing comprising a plurality of fibres and a UVR absorber, wherein the plurality of fibres have a density of less than 200 grams per square metre and the SPF rating of the article has been increased to at least 20 by the addition of less than 3% UVR absorber on weight of fibre.

Preferably, in the article of clothing comprising a plurality of fibres and a UVR absorber, wherein the plurality of fibres have a density of less than 200 grams per square metre, the SPF rating of the article has been increased to at least 20 by the addition of less than 2% UVR absorber on weight of fibre.

According to another aspect of the present invention, there is provided an article of clothing comprising a plurality of fibres and a UVR absorber of compound of formula (I)-(IV).

Preferably, in the article of clothing with the UVR absorber of compounds of formula (I)-(IV), the plurality

of fibres has a density of less than 200g/m².

Preferably, in the article of clothing with the UVR absorber compound of formula (I)-(IV) wherein the plurality of fibres have a density of less than 200g/m²,
5 the SPF rating of the article has been increased to at least 20 by the addition of less than 3% UVR absorber on weight of fibre.

More preferably, in the article of clothing with the UVR absorber compound of formula (I)-(IV) wherein the
10 plurality of fibres have a density of less than 200g/m², the SPF rating of the article has been increased to at least 20 by the addition of less than 2% UVR absorber on weight of fibre.

Preferably, the fibre comprising the UVR absorber is
15 colour-fast and light-fast.

Typically, the UVR absorber is bonded to the fibre by virtue of the reaction of compounds of formula (I)-(IV) with the fibre.

The present invention also provides a formulation
20 suitable for application to cellulosic or protein fibres or fabrics comprising a compound of formula (I)-(IV) in a suitable carrier.

Preferably, the SPF rating is increased to greater than 30.

25 It is preferred that the combination of fibre or fabric and UVR absorber is water-fast so that washing of the fabric after its SPF rating has been increased by the addition of the UVR absorber compounds of formula (I)-(IV), does not cause any significant drop in the SPF
30 rating of the fibre or fabric.

The fibre or fabric may also comprise a dye or pigment or other coatings or finishes known in the industry.

It is preferred that the UVR absorber be transparent
35 to visible radiation when applied to the fibre or fabric. Typically, once applied the original colour of the fabric or fibre is substantially unaffected.

The combination of fabric and UVR absorber is

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preferably light-fast. The fibre or fabric treated with the UVR absorber is preferably colour-fast to washing.

The fibre may be wool, nylon, polyester, cotton or any other synthetic fibre or composite thereof.

5 Preferably the UVR absorber is bonded to the fibres by virtue of an affinity the UVR absorber has for the fibres.

Preferred embodiments of the present invention will now be described by way of example only with reference to
10 the accompanying experimental results.

Best Modes for Carrying Out the Invention

SYNTHESIS METHODS

Example 1.

Synthesis via 1,3,5-s-triazine (cyanuric chloride)

15 The selected amine compound (1 mole as a slurry in 100 ml water [ice cold]) is added slowly to cyanuric chloride (1 mole as a slurry in 200ml acetone [ice cold]), whilst maintaining the pH of the solution at 7 by the addition of 2N sodium hydroxide. The reaction
20 mixture is stirred for 1.5-2.0 hours (whilst maintaining the temperature below 5°C) after which time the reaction is judged to be complete once the pH stabilises at 7 and the test for free amine (TLC) is negative. The product is then filtered off, washed thoroughly with acetone and
25 then oven dried.

Example 2.

Synthesis via 2,4,6-trifluoro-5-chloro-pyrimidine

The selected amine compound (1 mole as a slurry in 100 ml water [ice cold]) is added slowly to 2,4,6-
30 trifluoro-5-chloro-pyrimidine (1 mole dissolved in 300ml acetone [ice cold]), whilst maintaining the pH of the solution at 7 by the addition of a saturated aqueous solution of sodium carbonate. The reaction mixture is stirred for 1.5-2.0 hours (whilst maintaining the
35 temperature below 5°C) after which time the reaction is judged to be complete once the pH stabilises at 7 and the test for free amine (TLC) is negative. The product is then filtered off, washed thoroughly with acetone and

then oven dried.

Example 3.

Synthesis via epichlorohydrin

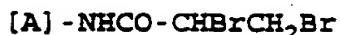
The selected amine compound (1 mole as a slurry in
5 100 ml ethanol [ice cold]) is added slowly to
epichlorohydrin (1 mole dissolved in 100ml ethanol [ice
cold]), whilst maintaining the pH of the solution at 7 by
the addition of a saturated aqueous solution of sodium
carbonate. The reaction mixture is stirred for 1.5-2.0
10 hours (whilst maintaining the temperature below 5°C)
after which time the reaction is judged to be complete
once the pH stabilises at 7 and the test for free amine
(TLC) is negative. The product is then filtered off,
washed thoroughly with acetone and then oven dried.

15 Example 4.

Synthesis via 2,3-dibromopropionic acid chloride

2,3-dibromopropionic acid chloride (1 mole) is added
dropwise to a solution of the selected amine (1 mole as a
slurry in 100 ml acetone containing 0.5 mole pyridine) at
20 30-45°C. The reaction mixture is then stirred for 14
hours at room temperature. The pyridine and acetone
solvents are then removed by vacuum evaporation.

The intermediate 2,3-dibromopropionamide compound:



25 is then treated as follows:

1 mole of the 2,3-dibromopropionamide compound is
charged into 500ml ethanol and heated to 60°C. Then add
dropwise a solution consisting of 1.6 mole of potassium
hydroxide in 250 ml ethanol. The temperature of the
30 reaction vessel is then raised from 60 to 68°C. Upon
completion of the addition, the reaction mixture is
heated under reflux for 4 hours.

Example 5.Synthesis of 2,4-dichloro-s-triazin-6-yl-p-aminophenyl-sulphonic acid sodium salt (dihydrate)

5 p-aminophenyl-sulphonic acid (sulphanilic acid) (26g as a slurry in water) was added slowly to cyanuric chloride (28g as a slurry in 200ml acetone containing circa 100g ice), whilst maintaining the pH of the solution at 7 by the addition of 2N sodium hydroxide. The reaction mixture was stirred for 1.5-2.0 hours after 10 which time the reaction was judged to be complete once the pH had stabilised at 7 and the test for free amine (TLC) was negative. The product was filtered off, washed thoroughly with acetone and then oven dried. The yield was 92%.

15 TLC showed that the product was free of starting materials. The IR spectrum and elemental analysis results confirmed the authenticity of the product. The elemental analysis results are given in the following table.

	Carbon	Hydrogen	Nitrogen
20 Expected	27.40	1.72	21.30
Found	27.53	1.84	21.25

Example 6.Synthesis of 2,4-dichloro-s-triazin-6-yl-amino-8-naphthol-3,6-disulphonic acid sodium salt (dihydrate)

25 38g 1-amino-8-naphthol-3,6-disulphonic acid was dissolved in 1N sodium bicarbonate solution, the solution was diluted to 500 ml and neutralised with acetic acid. This solution and 2N sodium bicarbonate solution were dropped simultaneously into a well stirred suspension of 30 cyanuric chloride (20.2g) in acetone and ice water (100ml 1:1) at 0°C over 3 hours. The reaction was judged to be complete when the pH stabilised at 7 and the test for free amine (TLC) was negative. The reaction solution was rotary evaporated (at 40°C) to reduce solvents. The 35 product was then filtered off and vacuum dried at room

temperature. The yield was 70%.

TLC showed that the product was free of starting materials. The IR spectrum and elemental analysis results confirmed the authenticity of the product. The
5 elemental analysis results are given in the following table.

	Carbon	Hydrogen	Nitrogen
Expected	33.42	1.72	11.99
Found	32.98	1.31	11.45

Characterisation of Products

10 The products were characterised using a combination of melting points, Infra-red [IR] spectra, elemental analyses and thin layer chromatography [TLC]. Melting points were determined on a Gallenkamp Melting Point Apparatus. IR spectra were recorded on a Hitachi Model
15 260-10 Infrared Spectrophotometer and referred to Nujol mulls. Elemental analyses were conducted (under contract) by the School of Chemistry, University of New South Wales. TLC was carried out using Merck 60F₂₅₄ Silica Gel TLC foils. A variety of eluents including
20 acetone, water-saturated butanol and ethanol were used. The chromatograms were visualised at 254nm with a Universal UV Lamp (CAMAG Muttenez Schweiz).

APPLICATION METHODS

1. Di-chloro-s-triazine UV absorber derivatives on cotton

25 Example 7.

These compounds may be applied to cotton by either exhaustion or pad methods

A suitable exhaustion method is as follows:

30 Apply 2% owf absorber compound, 10% owf sodium chloride and 0.1% owf wetting agent (e.g. a nonylphenyl polyethoxylate); LR 30:1; for 30 minutes at 30°C. Then add 5% owf sodium carbonate and run for 30 minutes. Finally wash off and dry.

35 The title compounds fix to the cotton via covalent bonds and hence provide a permanent increase in the SPF

of the treated cotton fabric.

Example 8.

A suitable pad-batch method is as follows:

5 Apply a solution containing 2% owf absorber compound, 5% owf sodium carbonate and 0.1% owf wetting agent (e.g. a nonylphenyl polyethoxylate) by padding to achieve a pick-up of 100%. The padded fabric is then batched (cold) overnight in a sealed plastic wrap. Finally wash off and dry.

10 The title compounds fix to the cotton via covalent bonds and hence provide a permanent increase in the SPF of the treated cotton fabric.

Example 9.

15 A suitable alternative pad-batch method is as follows:

Apply a solution containing 2% owf absorber compound, 5% owf sodium carbonate and 0.1% owf wetting agent (e.g. a nonylphenyl polyethoxylate) by padding to achieve a pick-up of 100%. The padded fabric is then
20 steamed for 30 minutes at 100-105°C to achieve fixation. Finally wash off and dry.

The title compounds fix to the cotton via covalent bonds and hence provide a permanent increase in the SPF of the treated cotton fabric.

25 2. Di-fluoro-mono-chloro-pyrimidine UV absorber derivatives on wool

Example 10.

These compounds may be applied to wool by either exhaustion or pad methods.

30 A suitable exhaustion method is as follows:

Apply 2% owf absorber compound, 10% owf sodium sulphate, 1.0% owf acetic acid and 0.1% owf wetting agent (e.g. a nonylphenyl polyethoxylate); LR 30:1. Start at 40°C, raise to 70°C over 20 minutes, hold at 70°C for 30
35 minutes; then raise the temperature to the boil and boil for 15 minutes. Finally wash off and dry.

The title compounds fix to the wool via covalent bonds and hence provide a permanent increase in the SPF

of the treated wool fabric.

Example 11.

A suitable alternative pad-batch method is as follows:

5 Apply a solution containing 2% owf absorber compound, 5% owf urea and 0.1% owf wetting agent (e.g. a nonylphenyl polyethoxylate) by padding to achieve a pick-up of 100%. The padded fabric is then steamed for 30 minutes at 100-105°C to achieve fixation. Finally wash
10 off and dry.

The title compounds fix to the wool via covalent bonds and hence provide a permanent increase in the SPF of the treated wool fabric.

In each of the following examples, a substance was
15 applied to a fabric of less than 200g/m² and the resultant combination was tested to obtain measurements on the change in SPF, whether the combination exhibited colourfastness to washing and whether the combination exhibited colourfastness to light.

20 UVR and SPF Measurement Methods

The ultra-violet transmission (direct and diffuse) of the sample was measured over the UVR spectral range of 290 to 380nm using a Cary 3 UVR-visible spectrophotometer fitted with an integrating sphere attachment. A Schott
25 UG#11 filter was used to eliminate the effects of fluorescence from the fluorescent whitening agents (FWA) (if any) in the sample.

The SPF's (sun protection factors) were estimated for 2mm "off skin" by a method developed in a research
30 project initiated by the Lidcombe Hospital Dermatology Center. The method is fully described in the publication entitled: "A Comparative Study of Fabric Protection against Ultraviolet-Induced Erythema Determined by Spectrophotometric and Human Skin Measurements", by S W
35 Menzies, P B Lukins, G E Greenoak, P J Walker, M T Pailthorpe, J M Martin, S K David and K E Georgouras, Journal of Photodermatology, Photoimmunology and Photomedicine, 1992: 8(4), 157-163.

The ultra-violet transmission data, and the calculated SPF's, were measured on the fabric in a dry relaxed state (i.e. not stretched).

The predicted SPF's are indicative of the SPF's to be found on human skin.

Colourfastness to washing

The colourfastness to washing of the untreated fabrics and UVR absorber treated fabrics was determined by the methods described in AS 2001.4.15 "Determination of Colourfastness to Washing: Test A: Colourfastness to Simulated Hand Laundering in the Presence of Soap".

Colourfastness to Light

The colourfastness to light of the untreated and UVR absorber treated fabrics was determined by the methods described in AS 2001.4.21 "Determination of Colourfastness to Light using an Artificial Light Source (Mercury Vapour, Tungsten Filament, Internally Phosphor-Coated Lamp)". Exposures were conducted for a total of 858 hours (circa 35 days) for which the ISO Blue Standard Rating was 7.

Details of all the chemicals mentioned in the specification are available from the indicated proprietor.

And extensive search of the literature and enquires made of textile chemical suppliers in Australia showed that there a very few water-soluble (or water-dispersable) UV absorbers commercially available.

There are no UV absorbers commercially available for cotton.

Ciba-Geigy market two UV absorbers:

CIBAFast N, which is described as "an agent to protect polyamide fibres against detrimental effects of light and heat and to improve the light fastness of dyeings of these fibres.

CIBAFast W, which is described as "an agent to protect wool against detrimental effects

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of light and heat".

Sandoz market one UV absorber for polyester:

5 FADEX F LIQUID, which is used to improve the
light fastness of dyeings of polyester,
particularly those used in automobile
upholstery.

Neither manufacturer makes any claim in their
technical literature regarding the use of these products
to increase the SPF of fibre or fabric.

10 EXAMPLE 12

Cibafast W (CFW) on wool.

Cibafast W is applied according to the exhaustion
method. Firstly, it is dissolved in a bath and the
product (fabric/fibre) has a wetting agent applied to it
15 before it is inserted into the bath. The bath is boiled
for approximately 1 hour to enable the Cibafast W to
enter the fabric/fibre.

Utilising the above method, it is noted that
Cibafast W is not glued to the fabric but instead enters
20 the fibres of fabric and in effect is bonded to the
fibres due to the affinity between Cibafast W and the
wool fibres.

In all the following examples, the "blank dyed"
samples referred to are samples that have been put
25 through the identical application process used for the
relevant UVR absorber, but without the active agent (UVR
absorber). The "blank dyed" sample often exhibits an
improved SPF due primarily to shrinkage effects incurred
in the process.

30 Using the application method described above, the
following results were obtained.

The stated "Suggested SPF" is the mean SPF less the
95% confidence limit rounded down to the nearest multiple
of five. Thus the suggested SPF is conservative.

TABLE 1

FABRIC DETAILS	SPF RESULTS (8 Samples)	SUGGESTED SPF
Control Wool Repeat	42 ± 12 34 ± 9	25+ 25+
Blank Dyed Repeat	64 ± 9 84 ± 30	55+ 50+
1% CFW	108 ± 19	85+
2% CFW	108 ± 20	85+
5% CFW	127 ± 26	100+
10% CFW	102 ± 18	80+

From Table 1 it is apparent that Cibafast W has caused a significant improvement in the SPF ratings for this wool fabric. An application of 1% CFW is sufficient to double the blank dyed SPF value.

The fastness of Cibafast W on wool to washing and light is given in the following Table 2.

TABLE 2

FABRIC DETAILS	INITIAL SPF	SPF AFTER WASHING	SPF AFTER 858 HOURS EXPOSURE
Control Wool	36 ± 3 (30+)	42 ± 18 (20+)	59 ± 20 (35+)
Blank Dyed	84 ± 30 (50+)	99 ± 29 (70+)	135 ± 40 (95+)
1% CFW	130 ± 50 (80+)	125 ± 34 (90+)	198 ± 112 (85+)
2% CFW	174 ± 76 (95+)	180 ± 85 (90+)	147 ± 26 (100+)

From Table 2 it is apparent that the improved SPF ratings obtained by using Cibafast W are "fast" to both washing and to light.

EXAMPLE 13Fadex F on PolyesterMethod of Application

Fadex F was first applied to polyester at 100°C in a
5 Goodbrand - Jeffries Dyemaster machine (S/N 13011)
Laboratory Dyeing Machine. However, it was noted that
polyester required an increased temperature in order to
effectively be impregnated with Fadex F. Accordingly,
Fadex F was applied at 130°C in the Labortex "Rapid"
10 Dyeing Machine Model #8. A person skilled in the art
would be familiar with such a method.

The results of impregnating polyester with Fadex F
are provided in Table 3.

TABLE 3

15	FABRIC DETAILS	SPF RESULTS (4 Samples)	SUGGESTED SPF
	Control PES	15 ± 1	10+
	Repeat	15 ± 2	10+
	Blank Dyed	18 ± 2	15+
	1% Fadex	39 ± 4	35+
20	2% Fadex F	48 ± 7	40+
	5% Fadex F	47 ± 8	35+

From Table 3 it is apparent that Fadex F causes a
significant improvement in the SPF ratings of polyester
fabric.

25 Fadex F was then tested for fastness to washing and
light.

TABLE 4

FABRIC DETAILS	INITIAL SPF	SPF AFTER WASHING	SPF AFTER 858 HOURS EXPOSURE
Control PES	15 \pm 1 (10+)	15 \pm 2 (10+)	18 \pm 4 (10+)
Blank Dyed	18 \pm 2 (15+)	19 \pm 5 (10+)	not tested
1% Fadex F	39 \pm 4 (35+)	37 \pm 3 (30+)	38 \pm 3 (30+)
2% Fadex F	48 \pm 7 (40+)	45 \pm 4 (40+)	49 \pm 6 (40+)
5% Fadex F	47 \pm 8 (35+)	52 \pm 7 (40+)	44 \pm 8 (35+)

From the data given in Table 4, it is apparent that the improved SPF ratings endowed by Fadex F on polyester are fast to both washing and exposure to light.

EXAMPLE 14

Fadex F on Nylon

Because a temperature of 130°C was required for the application of Fadex F to polyester, Fadex F was applied to nylon at 130°C centigrade in the Labortex "Rapid" Dyeing Machine.

The results of the application of Fadex F to nylon at 130°C centigrade indicated that the colour of the nylon was effected and accordingly, a temperature of 100°C was then adopted.

The Fadex F was thus applied to nylon at 100°C centigrade in the Dyemaster Dyeing Machine and was applied at 1% and 2% treatment levels. The treated nylon samples were only slightly yellowish in hue after the treatment. The results of the treatment of nylon with Fadex F are given in Table 5.

TABLE 5

FABRIC DETAILS	INITIAL SPF	SPF AFTER WASHING	SPF AFTER 858 HOURS EXPOSURE
Control Nylon Repeat	10 ± 3 (5+) 9 ± 1 (5+)	15 ± 1 (10+)	10 ± 2 (5+)
Blank Dyed	16 ± 2 (10+)	14 ± 1 (10+)	14 ± 3 (10+)
1½ Fadex F	29 ± 8 (20+)	28 ± 2 (25+)	21 ± 5 (15+)
2½ Fadex F	29 ± 6 (20+)	31 ± 10 (20+)	28 ± 6 (20+)

From Table 5 it can be seen that Fadex F significantly improves the SPF ratings of the nylon fabric employed. In addition, the results indicate that the improvement in SPF ratings caused by the addition of Fadex F is fast to both washing and exposure to light.

EXAMPLE 15

Fadex F on 65/35

Fadex F was applied to 65/35 polyester/cotton fabric at 130°C in the Labortex "Rapid" dyeing machine. The results are given in Table 6.

TABLE 6

FABRIC DETAILS	SPF RESULTS (4 samples)	SUGGESTED SPF
Control PES/CO	15 ± 2	10+
Blank Dyed	15 ± 5	10+
1½ Fadex	28 ± 6	20+
2½ Fadex F	25 ± 5	20+
3½ Fadex F	24 ± 4	20+

From Table 6 it is apparent that Fadex F causes a

significant improvement in the SPF ratings of this polyester/cotton fabric. The Fadex F treated fabric, were then assessed for fastness to washing and to light. The results are given in Table 7.

5 **TABLE 7**

FABRIC DETAILS	INITIAL SPF	SPF AFTER WASHING
Control PES	15 ± 2 (10+)	NOT TESTED
Blank dyed	15 ± 5 (10+)	15 ± 1 (10+)
1% FADEX F	28 ± 6 (20+)	27 ± 5 (20+)
10 2% FADEX F	25 ± 5 (20+)	26 ± 4 (20+)
3% FADEX F	24 ± 4 (20+)	24 ± 4 (20+)

From Table 7 it is apparent that Fadex F when applied to 65/35 polyester/cotton improves the SPF ratings and the SPF ratings are fast to washing.

15 Additional experimentation also indicates that the SPF ratings are fast to exposure to light with the SPF after 858 hours exposure being maintained at 20+.

EXAMPLE 16

20 Fadex F was also applied to secondary cellulose acetate and triacetate and as with nylon provided increases in SPF ratings similar to those provided for nylon. The Dyemaster Dyeing Machine method of application was also found to be suitable.

25 From the above experiments it is apparent that light weight materials of less than 200 grams per square metre, such as nylon, wool and polyester can be provided with significantly increased values of SPF protection by the addition of either Cibafast W or Fadex F as previously

outlined. The resultant and combination of fibre material and UVR absorber is both fast to washing and to exposure to light.

Both Cibafast W and Fadex F are UVR absorbers and have previously been used to protect particular fibres against detrimental effects of light and heat. From a vast number of different chemical substances it has been found that Cibafast W and Fadex F increased the SPF rating of the previously mentioned fibres to which they were applied, and at the same time avoided deleterious effects to the fibres. Other chemical substances used, for example, Cibafast N (a registered trade name of CIBA-GEIGY) not only failed to increase the SPF rating of the treated fabric but in many cases adversely affected the colour of the fabric so that it would be unsuitable for use commercially.

TABLE 8

SAMPLE	SPF RESULTS (8 Samples)	SUGGESTED SPF
Untreated Fabric	9 ± 1	5+
Blank Dyed	14 ± 2	10+
1% Cibafast N	17 ± 1	15+
2% Cibafast N	16 ± 2	10+

Table 8 provides the results of applying Cibafast N to nylon using the Dyemaster Laboratory Dyeing machine. From Table 8 it is apparent that Cibafast N did not significantly increase the SPF rating of the treated fabric and experiments also revealed that the Cibafast N induced a "greenish" colour into the white nylon fabric.

EXAMPLE 17Application of Compound 1 on cotton

(Compound 1 is 2,4-difluoro-5-chloro-6-phenylamino pyrimidine)

Compound 1 was prepared by the condensation of aniline (Fluka) and 2,4,6-trifluoro-5-chloropyrimidine

(Sandoz) by the method of Example 2.

17(a) Compound 1 was applied to 3g samples of a woven plain weave cotton fabric (145 g/m² : Charles Parsons, Sydney) by exhaustion from ethanol. The formulation was
5 as follows:

	1%	o.w.f. Compound 1		
	LR:	30:1		
	Temp:	20°C		
	Time:	10 minutes		
10	Cure:	Fan forced over;	90°C;	15 minutes.
	Wash:	Thorough cold rinse; then hot rinse (60°C)		
15	Dry:	Fan forced oven;	60°C;	30 minutes.

The results are summarized in the Table 9.

TABLE 9 : SPF RESULTS FOR WOVEN FABRIC

SAMPLE DETAILS	SPF RESULTS	SUGGESTED SPF
100% cotton control (4)	28.0 ± 3.2	20+
20 1% Compound 1 (8)	51.3 ± 7.7	40+

These preliminary small scale experiments show that Compound 1 has the capability of significantly increasing the SPF of this 100% cotton woven fabric.

17(b) Compound 1 was applied to 3g samples of a woven
25 plain weave cotton fabric (145 g/m² : Charles Parsons, Sydney) by exhaustion from aqueous emulsion. The formulation was as follows:

1%	o.w.f. Compound 1 (emulsion)
LR:	40:1

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Temp: Start at 40°C, Raise to 65°C
over 30 minutes; hold 30
minutes; raise to 98°C, hold 30
minutes.

5 Wash: Thorough cold rinse; then hot
rinse (60°C)

Dry: Fan forced oven; 60°C; 30
minutes.

The results are summarized in the Table 10.

10 **TABLE 10 : SPF RESULTS FOR WOVEN FABRIC**

SAMPLE DETAILS	SPF RESULTS	SUGGESTED SPF
100% cotton control (4)	28.0 ± 3.2	20+
Blank Treated (4)	26.6 ± 2.7	20+
1% Compound 1 (8)	42.6 ± 8.5	35+
15 2% Compound 1 (4)	44.4 ± 4.9	35+

These small scale experiments show that Compound 1 has the capability of significantly increase the SPF of this 100% cotton woven fabric.

UV-Transmission

20 The UV-transmission of a 5g/l ethanolic solution of Compound 1 was measured in a 5mm quartz cell using a Cary 3 UV-Visible spectrophotometer.

The results are given in Figure 1.

25 It can be readily seen that Compound 1 begins to absorb strongly below 340nm; ie in the UVB region. Thus this type of compound absorbs the very harmful UVB rays YET will not significantly interfere with the function of fluorescent whitening agents (FWA). Thus the treated cotton remains a full white.

30 On the basis of these results it can be seen that 1% o.w.f. Compound 1 gives a very significant increase in the SPF of this 100% cotton fabric.

EXAMPLE 18Application of Compound 2 on Cotton

(Compound 2 is p-(2,4-dichloro-s-triazine-6-ylamino)-o-methyl-phenyl sulphonic acid sodium salt)

5 In the following application recipe it has been assumed that Compound 2 has been formulated as 100% reactive compound.

10 In the determination of wash-fastness of the treated fabric, soap was replaced by 1g/l of OMO (OMO is a trade mark of Unilever plc).

18(a) Compound 2 was applied to 5g samples of woven plain weave 100% cotton fabric (145g/m² : Charles Parsons, Sydney) by exhaustion in a Goodbrand-Jeffries Laboratory Dyeing Machine. The formulation was as follows:

15 50 g/l Sodium chloride (NaCl)
 x% o.w.f. Compound 2
 LR 40:1
 Temp: 50°C
 Time: 30 minutes

20 Then: Add 5 g/l Sodium carbonate
 Run: 30 minutes of 50°C
 Wash: Thorough cold rinse; then
 hot rinse (60°C)

25 Dry: Fan forced over; 60°C; 60
 minutes.

The results are summarized in the Table 11.

TABLE 11 : SPF RESULTS FOR WOVEN FABRIC

SAMPLE DETAILS	SPF RESULTS	SUGGESTED SPF
100% cotton control (4)	29.5 ± 2.6	25+
Blank treated sample (4)	26.4 ± 7.3	15+
1% Compound 2 (8)	41.1 ± 5.6	35+
2% Compound 2 (8)	47.7 ± 11.8	35+

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These preliminary small scale experiments show that Compound 2 has the capability of significantly increasing the SPF of this 100% cotton woven fabric.

18(b) Winch Application

5 3% Compound 2 was applied to 600g of a woven plain weave 100% cotton fabric (Charles Parsons, Sydney) by exhaustion in a laboratory scale winch dyeing machine. The formulation was as follows:

10	50 g/l Sodium chloride (NaCl)	
	3%	o.w.f. Compound 2
	LR	30:1
	Temp:	50°C
	Time:	30 minutes
	Then:	Add 5 g/l Sodium carbonate
15	Run:	30 minutes of 50°C
	Wash:	Thorough cold rinse; then hot rinse (60°C)
	Dry:	Tumble dry: 60°C; 60 minutes.

20 The results are summarized in the Table 12.

TABLE 12 : SPF RESULTS FOR WOVEN FABRIC

SAMPLE DETAILS	SPF RESULTS	SUGGESTED SPF
100% cotton control (8)	24.5 ± 3.6	20+
3% Compound 2 (8)	41.0 ± 4.4	35+

25 These winch dyeing experiments show that Compound 2 has significantly increased the SPF of this 100% cotton woven fabric.

30 The fastness to washing and to light of the Compound 2 (winch) treated 100% cotton was then evaluated and the results are given in Table 13.

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TABLE 13 : FASTNESS RESULTS

	SAMPLE DETAILS	SPF RESULTS	SUGGESTED SPF
	100% cotton control (8)	24.5 \pm 3.6	20+
	3% Compound 2 (8)	41.0 \pm 4.4	35+
5	After 1 wash/drying cycle (8)	39.9 \pm 4.5	35+
	After 5 wash/drying cycle (8)	41.8 \pm 3.6	35+
	After 70 hours light exposure		
	Blank (Untreated) (8)	32.1 \pm 5.3	25+
	Treated (8)	50.1 \pm 12.2	35+
10	After 162 hours light (8) exposure	43.0 \pm 5.8	35+

18(c) Pad-Batch Application to knitted fabric

3% Compound 2 was applied to circa 35g of a knitted
 15 100% cotton fabric (Avon 100% cotton; Size XXL; Sunsafe
 30+ : This fabric would have a weight of 180-190 g/cm²)
 by padding using a laboratory scale padding machine. The
 formulation was as follows:

3% w/w Compound 2
 20 5 g/l sodium carbonate

Add-on: 90%
 Temp: Room temperature
 Batch: 6 hours (cold) in sealed
 plastic bags

25 Wash: Thorough cold rinse;
 then hot rinse (60°C)

Dry: Tumble dry: 60°C; 60
 minutes.

The results are summarized in the Table 14.

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TABLE 14 : PAD-BATCH RESULTS ON KNITTED FABRIC

SAMPLE DETAILS	SPF RESULTS	SUGGESTED SPF
100% cotton control (8)	33.7 \pm 5.7	25+
Blank padded sample (8)	51.5 \pm 4.5	45+
5 2.7% Compound 2 (8)	103.1 \pm 17.0	85+

The "blank" padded sample has shrunk, giving rise to the higher SPF of this specimen. The Compound 2 treated sample has a greatly improved SPF over both the control and blank samples.

These pad-batch dyeing experiments show that Compound 2 has significantly increased the SPF of the 100% cotton knitted fabric.

18(d) Pad-Batch Application to woven fabric

15 3% Compound 2 was applied to circa 25g of a woven 100% cotton fabric (Charles Parsons) by padding using a laboratory scale padding machine. the formulation was as follows:

20	3%	w/w Compound 2
		5 g/l sodium carbonate
	Add-on:	90% (Hence 2.7% applied)
	Temp:	Room temperature
	Batch:	6 hours (cold) in sealed plastic bags
25	Wash:	Thorough cold rinse; then hot rinse (60°C)
	Dry:	Tumble dry: 60°C: 60 minutes.

The results are summarized in the Table 15.

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TABLE 15 : SPF RESULTS FOR PADDED WOVEN FABRIC

SAMPLE DETAILS	SPF RESULTS	SUGGESTED SPF
100% cotton control (8)	24.5 ± 3.6	20+
Blank padded woven (8)	30.9 ± 4.5	25+
5 2.7% Compound 2 (8)	59.5 ± 6.9	50+

These pad-batch dyeing experiments show that Compound 2 has significantly increased to SPF of this 100% cotton woven fabric.

10 On the basis of these results it can be seen that Compound 2 can be conveniently applied to cotton fabrics (either knitted or woven) by both "exhaustion" and "pad-batch" methods.

15 The treated fabrics are fast to both washing and to light.

The treated fabrics have significantly higher SPFs than the control fabrics (and blank treated fabrics).

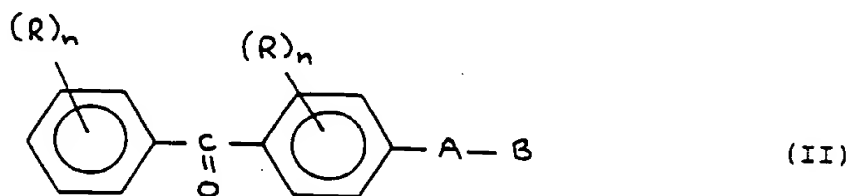
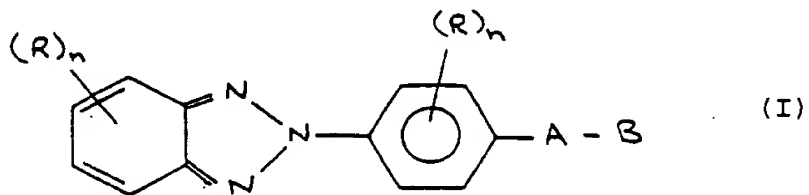
20 Compound 2 beings to absorb strongly below 359nm, ie in the UVB region. UVB is most damaging to the skin and the principal cause of skin cancer.

By not absorbing significantly above 350nm, Compound 2 does not inhibit the function of fluorescent whitening agents (FWA) and hence the fabric remains a bright white yet has a high SPF.

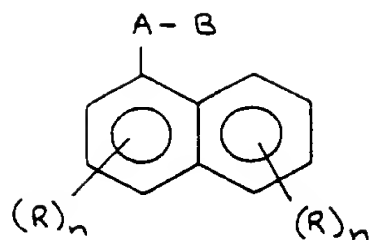
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Claims

1. A method of increasing the SPF rating of a fibre or fabric, comprising the steps of providing a UVR absorber, applying the UVR absorber to a fabric having a density of less than 200 grams per square metre, whereby the UVR absorber is attached to the fibre and an application of less than 3% UVR absorber on weight of fibre produces an SPF rating of greater than 20 for the UVR absorber and fabric combination.
2. A method according to claim 1 where an application of less than 2% UVR absorber on weight of fibre produces an SPF rating of greater than 20 for the UVR absorber and fabric combination.
3. A method of increasing the SPF rating of cellulosic or protein fibre or fabric, comprising applying to cellulosic or protein fibre or fabric one or more compounds of formula (I)-(IV):



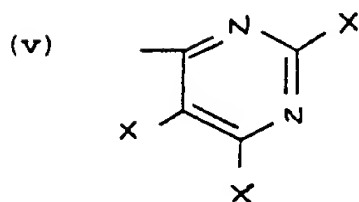
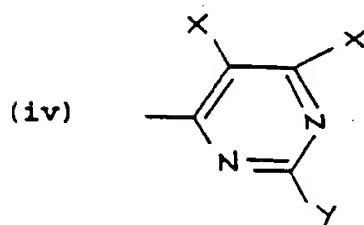
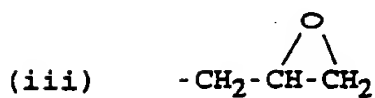
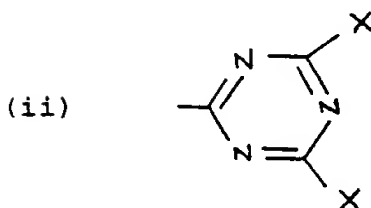
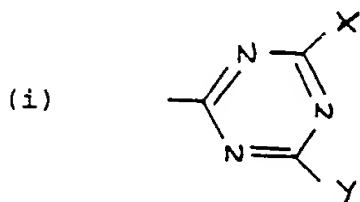
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(IV)

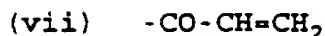
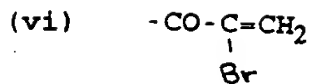
wherein A is -NH- or -SO₂- and when A is -NH-, B is selected from a compound of formula (i) - (vii) as follows:

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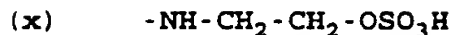
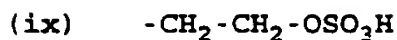
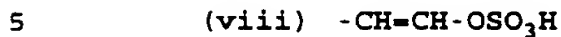


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and where A is $\text{-SO}_2\text{-}$, B is selected from a compound of formulae (viii) - (x) as follows:



10 wherein R is independently selected from -OH , -NH_2 , $\text{-SO}_3^-\text{M}^+$, $\text{-SO}_3\text{H}$, alkyl, alkoxy, alkanoyl, alkylcarboxylate, -S-alkyl , -CF_3 , -N-di-alkyl ;

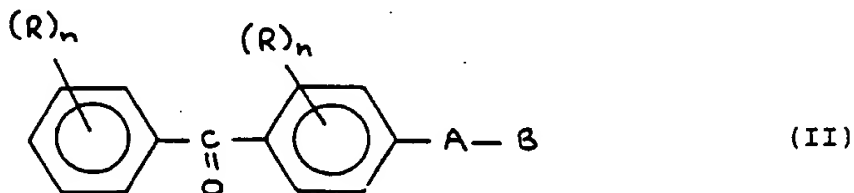
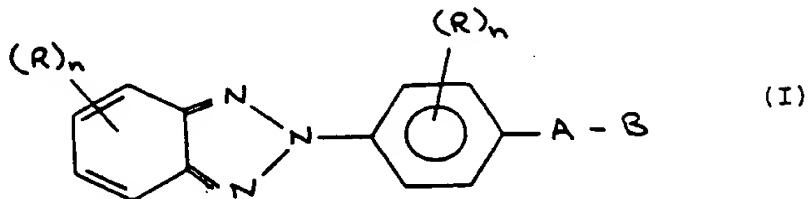
$n = 0, 1, 2, 3$ or 4

M^+ = cation

$\text{X} = \text{H}$, or Cl , F , Br and is independently selected

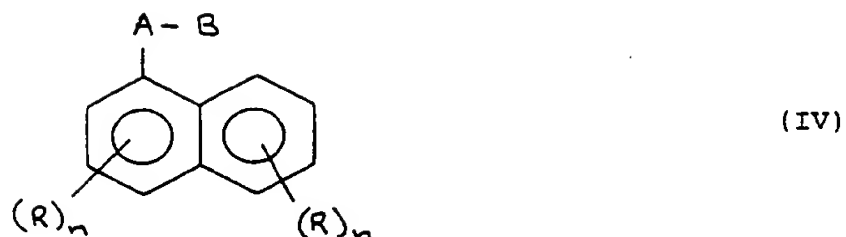
$\text{Y} = \text{X}$ or R .

15 4. A compound of formula (I), (II), (III) or (IV)



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wherein A, B, R and n are as defined in claim 3; but excluding the compound of formula (III) where A is -NH-,

- 5 B is a compound of formula (ii),
 X is Cl, n is 2 and one R is in the 3-position of the phenyl ring and is -CH₃ and the other R is in the 4- position and is -SO₃⁻ Na⁺.

5. A process of preparing a compound of formula (I)-(IV) as defined in claim 4 which comprises:

- 10 1) for preparing compounds of formula (I)-(IV) where A is -NH- and B is a compound of formula (i), (ii), (iii), (iv) or (v):
 reacting the appropriate amine of formula
 15 (I), (II), (III) or (IV) with a chloro derivative of a compound of formula (i), (ii), (iii), (iv) or (v);
- 2) for preparing compounds of formula (I)-(IV) wherein A is -NH- and B is a compound of
 20 formula (vi) or (vii):
- (i) reacting the appropriate amine of formula (I), (II), (III) or (IV) with -CH₂BrCHBrCOCl to provide the dibromopropionyl derivative;
- 25 (ii) debromination with potassium hydroxide or the like to provide the bromoacrylamido derivative of formula (vi); and
- (iii) further debromination with potassium
 30 hydroxide or the like to provide the acrylamido derivative of formula (vii);

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- 3) for preparing compounds of formula (I)-(IV) where A is $-SO_2-$ and B is a compound of formula (viii) or (ix):
- 5 (i) esterification of the appropriate β -hydroxyethyl sulphone derivatives of the compounds of formulae (I) to (IV) with sulphuric acid or the like to provide compounds of formula (I) to (IV) where B is a compound of formula (viii) and;
- 10 (ii) dehydration in the presence of a base to form the vinyl compound of formula (ix);
- 4) for preparing compounds of formula (I)-(IV) where A is $-SO_2-$ and B is a compound of formula (x):
- 15 esterification of the appropriate β -hydroxyethyl aminosulphone derivative of the compounds of formulae (I)-(IV) with sulphuric acid or the like (as in 3(i) above) to provide compounds of formula (I)-(IV) where B is a
- 20 compound of formula (x).
6. A method of increasing the SPF rating of cellulosic or protein fibre or fabric, comprising the steps of applying a compound of formula (I)-(IV) to cellulosic or protein fibres or fabric having a
- 25 density of less than $200g/m^2$ whereby an application of less than 3% of a compound of formula (I)-(IV) on weight of fibre or fabric produces an SPF rating of greater than 20.
7. A method according to claim 6 where an application
- 30 of less than 2% of a compound of formula (I)-(IV) on weight of fibre or fabric produces an SPF rating of greater than 20.
8. An article of clothing comprising a plurality of fibres and a UVR absorber, wherein the plurality of
- 35 fibres have a density of less than 200 grams per

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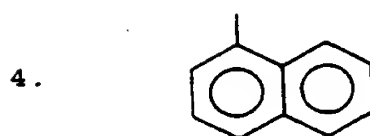
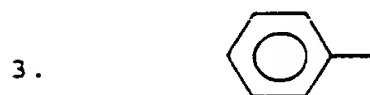
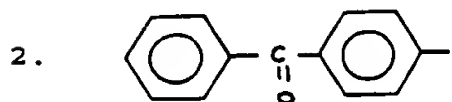
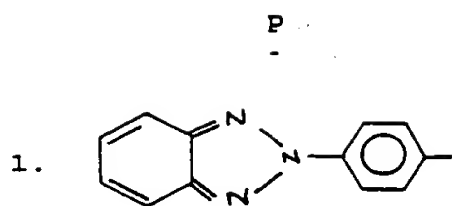
square metre and the SPF rating of the article has been increased to at least 20 by the addition of less than 3% UVR absorber on weight of fibre.

- 5 9. An article of clothing according to claim 8, wherein the SPF rating of the article has been increased to at least 20 by the addition of less than 2% UVR absorber on weight of fibre.
- 10 10. An article of clothing comprising a plurality of fibres and a UVR absorber compound of formula (I)-(IV).
11. A formulation suitable for application to cellulosic or protein fibre or fabric comprising a compound of formula (I)-(IV) in a suitable carrier.
- 15 12. A method according to claim 1 wherein the fabric is polyester and the UVR absorber is Fadex F.
- 20 13. A method according to claim 2 for increasing the SPF rating of cotton which comprises applying a compound of formula (III) where A is -NH-, B is a compound of formula (ii),
X is Cl, n is 2 and one R is in the 3-position of the phenyl ring and is -CH₃ and the other R is in the 4-position and is -SO₃⁻ Na⁺.
- 25 14. Clothing or fabric in which the SPF rating has been increased to 20 or more by a method according to claim 1 or 3.
15. A compound of formula (I), (II), (III) or (IV) according to claim 4 which is a compound of formula P-Q and is a combination of P as defined below with any Q as defined below:

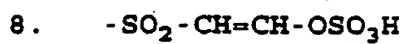
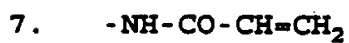
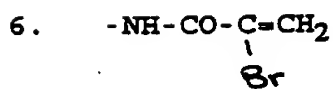
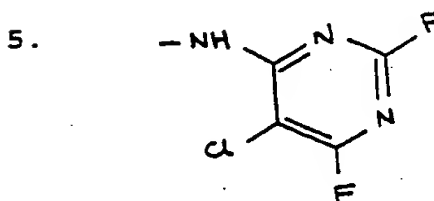
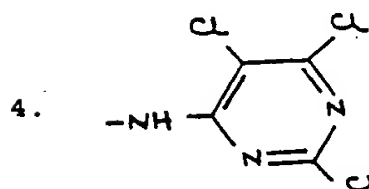
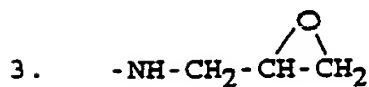
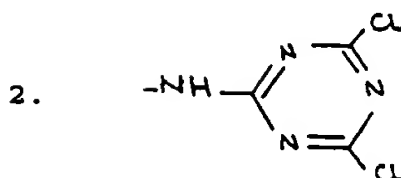
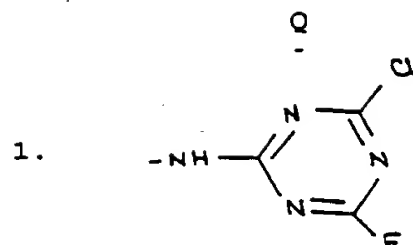
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P



Q



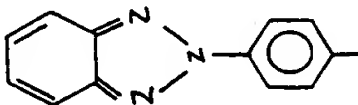
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16. A method according to claim 3 wherein the one or more compounds of formula (I)-(IV) is a compound of formula P-Q which is a combination of P as defined below with any Q as defined below:

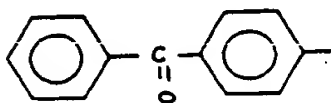
5

P

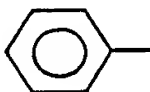
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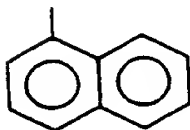
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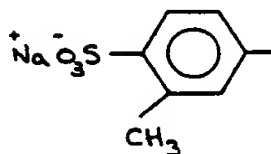
3.



4.

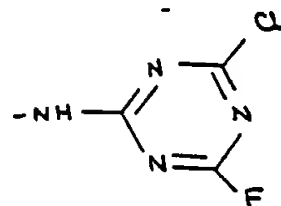


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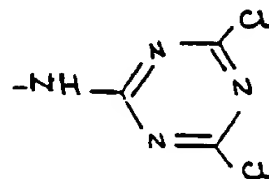


Q

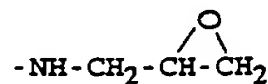
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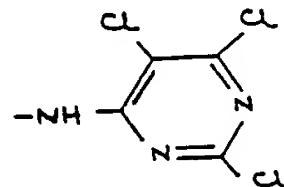
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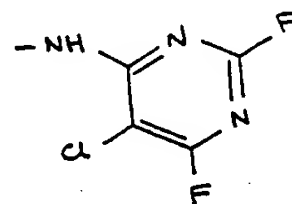
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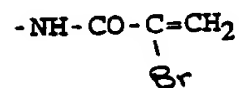
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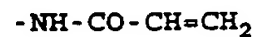
5.



6.



7.



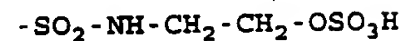
8.



9.



10.

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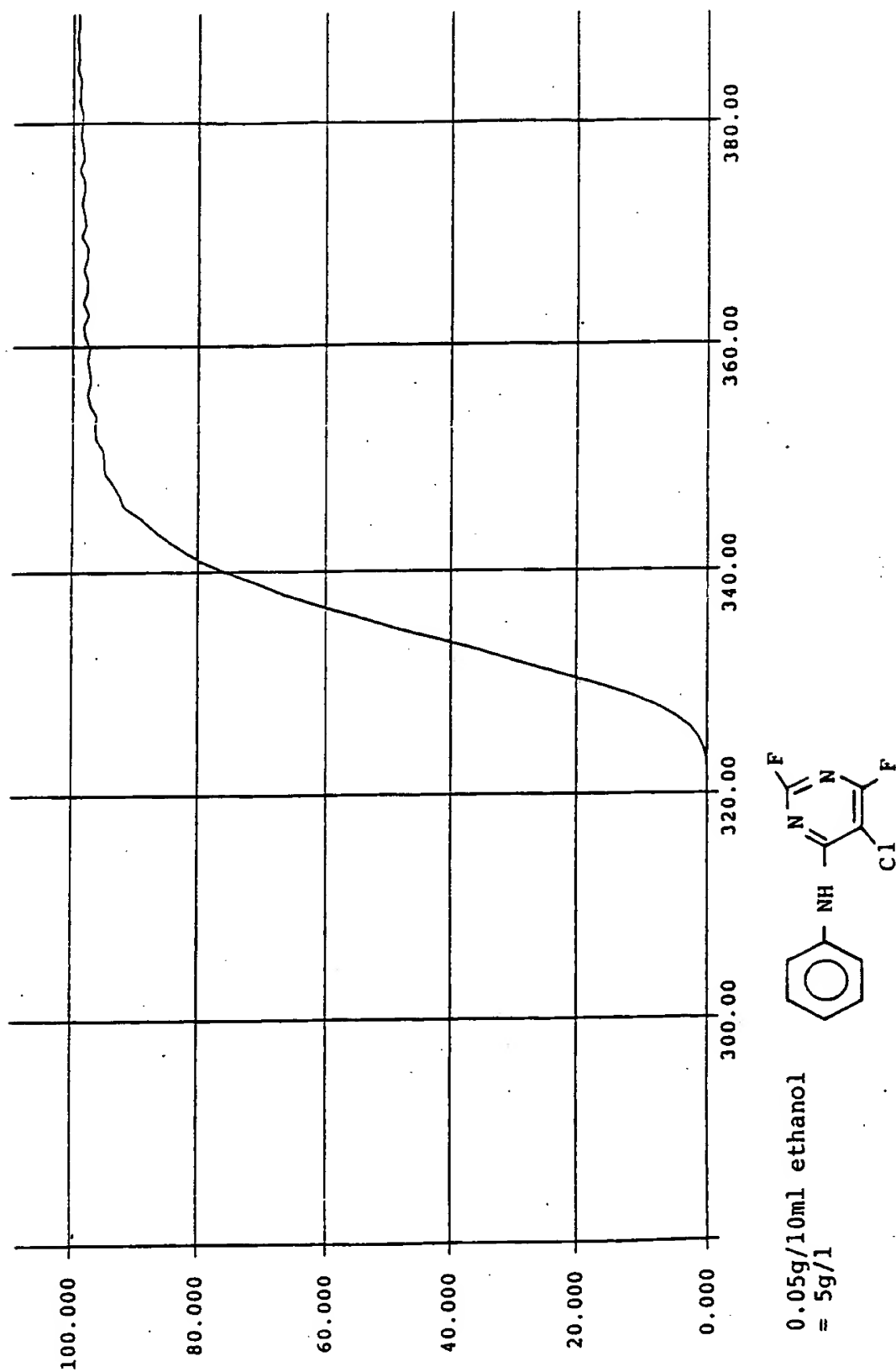



FIGURE 1

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A. CLASSIFICATION OF SUBJECT MATTER Int. Cl. ⁵ C07D 251/44, C07D 239/42, D06M 013/355, According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int. Cl. ⁵ C07D 251/44, C07D 239/42, D06M 013/355, Int. Cl. ⁴ D06M 013/38 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched AUSTRALIAN CLASS IPC and IPC AS ABOVE, JOPAL AS ABOVE Electronic data base consulted during the international search (name of data base, and where practicable, search terms used) DERWENT IPC AS ABOVE. CHEMICAL ABSTRACTS ONLINE SUBSTRUCTURE SEARCH				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.		
X	US,A, 2820032 (HILL et al) 21 April 1954 (21.04.54) Column 4, lines 14 to 20	4, 5, 15		
X	US,A, 2719846 (BURTNER) 6 May 1954 (06.05.54) column 2, line 52	4		
X	US,A, 2720480 (WOLF) 17 July 1953 (17.07.53) Examples III, V, XVI, XVII, and XXXI	4, 5, 15		
X	US,A, 3198797 (DEXTER et al) 21 February 1961 (21.02.61) Example 2.	4, 5		
<div style="display: flex; justify-content: space-between; align-items: flex-start;"> <div style="width: 45%;"> <input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. </div> <div style="width: 45%;"> <input type="checkbox"/> See patent family annex. </div> </div>				
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top;"> <p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </td> <td style="width: 50%; vertical-align: top;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p> </td> </tr> </table>			<p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>
<p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>			
Date of the actual completion of the international search <div style="text-align: center; font-family: cursive;">18 NOVEMBER 1993 (18.11.93)</div>		Date of mailing of the international search report <div style="text-align: center; font-family: cursive;">19 NOV 1993 (19.11.93)</div>		
Name and mailing address of the ISA/AU AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No. 06 2853929		Authorized officer <div style="text-align: center;">  C.A. BRICK Telephone No. (06) 283 2453 </div>		

Category *	Citation of document, with indication, where appropriate of the relevant passages	Relevant to Claim No.
X	US,A, 3666759 (CRABTREE) 3 August 1970 (03.08.70) Column 2 lines 8-14, 30-39, 54-62.	4, 5
X	GB,A, 872313 (FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT) 21 August 1957 (21.08.57) Examples 1 and 3	4
X	GB,A, 889292 (AMERICAN CYANAMID COMPANY), 11 June 1959 (11.06.59) Whole of document.	3 to 5, 10, 11
X	GB,A, 1444426 (SANDOZ LTD) 23 October 1972 (23.10.72) Example 1	3, 4, 10, 11
X	DE,A, 3330547 (BAYER AG) 24 August 1983 (24.08.83) Tables I, II, V, VII, VIII	4
X	EP,A 36133 (HOESCHT AG) 19 March 1980 (19.03.80) Examples 1, 2, 5, 6, 7	4
X	EP,A, 172790 (CIBA-GEIGY AG) 21 August 1984 (21.08.84) Pages 5, 8, 11	4, 5
X	EP,A, 213071 (CIBA-GEIGY AG) 30 July 1985 (30.07.85) Page 13; lines 19 to 22; Page 16, lines 3 to 16; Page 17 lines 5 to 18; Page 18 lines 8 to 21; Page 19 lines 11 to 24; Page 21, example 5	4, 5
X	EP,A, 298041 (CIBA-GEIGY AG) 2 July 1987 (02.07.87) Example 4	4, 5
X	DE,A, 3202120 (HOESCHT AG) 23 January 1982 (23.01.82) Examples 1, 2, 3 to 5, 12, 13 to 66	4, 5
X	DE,A, 3740650 (BAYER AG) 1 December 1987 (01.12.87) Examples 1, 2, 4, 5, 6, 7, 8; Page 5, lines 16 to 30	4, 5
X	EP,A, 542082 (BAYER AG) 13 November 1991 (13.11.91) Examples 1, 5	4, 5
X	BE,A, 859725 (CIBA-GEIGY AG) 15 October 1976 (15.10.76) Examples 1, 3, 6	4, 5
X	"The Chemistry and Application of Dyes", Edited by D.R. WARING AND G. HALLAS, Plenum Press, New York 1990. Page 87, lines 23 to 26.	4, 5
X	"The Chemistry of Heterocyclic Compounds, The Pyrimidines" D.J. Brown, Interscience Publishers 1962. Page 312, line 4; Page 191, line 28; Page 543, compounds 2, 4, 6	4, 5
	SUPPLEMENT 1, WILEY-Interscience Publishers 1970 Table XXXI, (T81), Compounds 10, 11	4, 5, 15
	SUPPLEMENT II, JOHN WILEY & SONS PUBLISHERS Page 570, compounds 17, 25; Page 571, compound 3	4, 5
X	"The Chemistry of Synthetic Dyes", Volume VI Reactive Dyes, Edited by K. Venkataraman Academic Press New York 1972. Page 37, Structure (III); Page 40 lines 6 to 9; Page 104, line 2; Page 105, lines 13 to 14; Page 133 line 2 to 4.	4, 5, 15

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international search report has not established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claim Nos.: 12
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

The exact structure of FADEX-F was not known to the examiner at the time of searching, and a meaningful search could not be carried out for this reason. Furthermore as FADEX-F is a trade composition, its ingredient may change imparting a different scope on claim 12.

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
US	3666759	CH GB	508025 1205016	CH	568305	DE	1644286
GB	1444426	BE ES NL	806372 419821 7314403	CH FR	15473/72 2203907	DE IT	2352465 1008582
DE	3330547	EP	134033	DFR	2562254	DUS	4649748
EP	36133	AR IN	230629 151896	BR US	8101594 4361698	DE	3010502
EP	172790	DE	3586409	KR	8700785	US	4740597
EP	213071	BR	8603583	DE	3662266	US	4855410
EP	298041	BR	8803273	US	4900813	US	4975530
DE	3202120	BR EP US	8300264 84849 4939243	CS IN	233744 157904	DE KR	3202120 9101701
EP	542082	DE	4137393				
END OF ANNEX							